

The University of Chicago

MIXED FILMS OF
SOME LONG CHAIN FATTY ACIDS
WITH HYDROCARBONS

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
JUNE, 1938

By
HAROLD M. SCHOLBERG

CHICAGO, ILLINOIS
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INTRODUCTION

Harkins and Myers^{1,2} made a rapid survey of some of the characteristics of mixed films of fatty acids and tetradecane, Nujol, and dotriacontane. They could not tell whether the films were homogeneous or not since the films were examined by eye only. In order, therefore, to test for inhomogeneity Fowkes, Myers and Harkins³ made a cursory examination of the same type of films using a microscope with dark field illumination.

In work which was reported at the Pittsburg meeting of the American Chemical Society, September, 1936, Harkins and Myers demonstrated that pentadecylic acid-Nujol force-area per molecule of acid curves showed a continuous shift to larger values of the area at zero force until a concentration of 32 per cent Nujol was reached, whereupon the area at zero force remained constant. A plot of the area at zero compression occupied by a milligram of the mixture against the percentage of Nujol showed an inflection point at 32 per cent oil.

Langmuir⁴ has developed a theory of expanded films which rests upon the concept of duplex layers. According to Langmuir, a film may be supposed to consist of two layers: one an extremely thin lens formed by the hydrocarbon tails of the molecules, the other layer formed of the active heads of the molecules. The heads may be regarded as an imperfect gas at the oil-water interface.

¹J. Phys. Chem., 40, 959 (1936).

²J. A. C. S. , 58, 1817 (1936).

³J. A. C. S., 59, 597 (1937).

⁴J. Chem. Phys., 1, 762 (1933).

Langmuir considered the film pressure, F , as the sum of a quantity F_0 due to the tails, and a quantity F_{12} due to the heads. F_0 was taken by Langmuir as the spreading coefficient of the hydrocarbon tails, that is,

$$F_0 = \gamma_1 - \gamma_2 - \gamma_{12}$$

where

γ_1 = surface tension of substrate
 γ_2 = surface tension of hydrocarbon
 γ_{12} = interfacial tension of hydrocarbon-substrate.

F_{12} was considered as an imperfect gas pressure,

$$F_{12} = kT/(a - a_0)$$

where a_0 corresponds roughly to the closest packing of the heads themselves. Substituting in the above equation for F , Langmuir obtained, for the equation of state of these "duplex" films,

$$(F - F_0)(a - a_0) = kT.$$

Langmuir proposed, as a test of this hypothesis, that the addition of a pure hydrocarbon to the film before it is spread would produce little change in the F - A curve other than that produced by a slight change in the F_0 value. He said: "Some preliminary experiments to test this point have shown that the addition of an equal weight of tetradecane to myristic acid produces no appreciable change in the F - A curves."

It was the purpose of this work to attempt to find the cause of the singular behavior of the pentadecylic acid-Nujol curves at the concentration of 32 per cent oil, and to attempt to test the validity of the Langmuir theory of expanded films.

APPARATUS

The surface tension balance used in this work was the Wilhelmy¹ type, a detailed analysis of which has been given by

¹Ann. Physik, 119, 177 (1863).

Harkins and Anderson.¹ The method consists in measuring directly, by means of a balance, the pull of the surface of the liquid on the perimeter of a body, such as a vertical microscope slide partially immersed in the liquid. With the slide hanging free in the liquid, equilibrium is set up, for which the following equation holds

$$gG = gW + 2\sigma(t + w)\cos \theta - g\rho ltw$$

where

w = width of slide
 t = thickness of slide
 θ = angle of contact of liquid with the slide
 σ = surface tension
 l = depth of immersion of slide
 g = acceleration of gravity
 ρ = density of liquid
 W = weight of free dry slide
 G = apparent weight of the partly immersed slide.

If the surface tension is changed while G is kept constant, we may write from the above equation

$$g\Delta G = 2(t + w)\Delta\sigma - g\rho t w \Delta l = 0.$$

In the last equation the assumption was made that θ equaled 0, which is true for a clean glass slide immersed in water. Under these conditions the change in surface tension is proportional to the change in the depth of immersion of the slide, which can be measured directly by means of a cathetometer. It was more convenient, however, to mount a galvanometer mirror on the beam of the balance and observe deflections of the beam by means of a telescope and illuminated millimeter scale. For small deflections of the beam Δl is proportional to ΔS , the change in the scale reading. This gives

$$g\Delta G = 2(t + w)\Delta\sigma - k\Delta S$$

where k is the factor of proportionality.

The calibration of the Wilhelmy balance consisted in

¹J. A. C. S., 59, 2189 (1937).

determining the proportionality factor k by noting deflections of the balance beam ΔS for added weights ΔG on the balance pan with the slide partially immersed in a clean water surface, $\Delta f = 0$. We then have the relation

$$k = -g\Delta G/\Delta S.$$

The reductions of the surface tension caused by spreading and compressing a film can then be determined by noting the beam deflections ΔS while the weight on the pan is kept constant, $\Delta G = 0$. The equation for the force exerted by the film is

$$F = -\Delta f = k\Delta S/2(t + w).$$

The microscope slide used was 25.469 mm. wide and 1.229 mm. thick. This was the average of six determinations. It was found that 1 cm. on the scale was equivalent to a change in surface tension of .4182 dynes.

The trough and barriers were made of brass. They were coated with paraffin. Ferric stearate was tried as a coating for the tray but was found to be unsatisfactory. The trough was made with a false bottom and was built in such a manner that all soldering was on the side away from the substrate for the film. The trough was built into a duraluminum case, the top of which was provided with two removable glass covers. An inch and a half hole was cut in the top of the case to allow a microscope to be adjusted over a cardioid condenser in the bottom of the trough. A carbon arc rated at 55 volts and 8 amperes furnished light for the microscope.

A compact air thermostat was built around the duraluminum case. The thermostat was made of unfinished masonite and lined with galvanized iron. Three doors were built into the thermostat, two on top and one on the end. These doors allowed complete access to the inside. In order to inspect the film with the microscope, it was necessary to have the microscope half inside and half out-

side the air thermostat. This was accomplished by means of an automobile inner tube cut to fit the microscope opening in the thermostat. The rubber piece had two holes cut in it, one of which fitted snugly around the tube of the microscope and the other around the supporting base immediately under the focussing knobs. By making the rubber sheet large it was found that the microscope could be moved around easily and focussed without difficulty.

In order to keep the temperature constant, air was circulated through coils immersed in a water thermostat, which was kept at constant temperature to a hundredth of a degree, and then through the air thermostat. The coils were made of four inch copper downspout and were filled with turnings. Two cotton filters, one at the inlet and the other at the outlet to the air thermostat, served to take out most of the dust raised by the moving air. The motor for moving the air was an ordinary hand vacuum cleaner motor mounted directly on the water thermostat. Air connections to the motor and to the air thermostat were of rubber, as were the motor mountings, in order to eliminate vibration as much as possible. Thermometer wells were placed ahead of and behind the motor and ahead of the air thermostat. The motor was placed ahead of the coils so that the air was pushed through the coils and into the thermostat. It was found that the motor raised the temperature of the air about eight degrees and that this was too much for the coils to regulate. A cooling coil, therefore, was placed in the outlet pipe just ahead of the motor.

Water from the water thermostat was pumped into a reservoir inside the air thermostat and from there allowed to flow by gravity through the false bottom trough and back to the water thermostat.

With this arrangement it was found that the temperature in the air thermostat could be kept constant to plus or minus .02 of

a degree for several hours, provided the room temperature did not change more than two degrees either way. Heat leakage around the microscope and temperature gradients inside the thermostat were the main sources of trouble. Little could be done about the leakage, but the temperature gradients were eliminated by the proper placement of baffles.

The analytical balance used to measure the differential pressure was mounted directly to the top of the air thermostat by means of a tripod which was braced with three stays of piano wire. A galvanometer mirror was mounted at the center point of the balance beam. By focussing a telescope on the mirror the reading on an illuminated scale on the wall could be estimated, with practice, to one-tenth of a millimeter. The apparatus was calibrated before each run and if the calibration was off by more than three-tenths of a per cent from the average, the surface was reswep and the slide recleaned. In calibrating the apparatus the weights were added without arresting the balance, since it was found that more consistent results could be obtained by this method than by arresting the balance before changing G. In other words, the smoothness of the curves depends on the sensitivity of the balance, while the absolute value of the force depends on the accuracy of the balance. In order to measure the area one of the push-rods which moved the compression barrier had a scale ruled on it which could be read by means of a vernier to one-tenth of a millimeter.

The slide was a microscope slide made of resistance glass. A short piece of slide, to serve as a damper, was fastened at right angles to the bottom of the slide with Nichrome wire. During a reading the slide would show a slow vibration of about one millimeter on the scale. It is imperative that the angle of contact of the water with the slide be constant and known: This means that

it must be clean. It was cleaned by boiling in concentrated sodium hydroxide for several hours. When not in use it was kept in a solution of tri-sodium phosphate.

In order to spread the film without opening the air thermostat more than was necessary, a hole three-fourths of an inch in diameter was cut in the glass cover of the duraluminum box directly under a four by six inch door in the top of the air thermostat.

The film was spread by means of the type of pipette described by Harkins and Anderson.¹

A brass pipe was put in place between the balance and the duraluminum box. This served to protect from disturbing drafts the copper wire which supported the glass slide and which hung from the balance arm.

MATERIALS

The fatty acids used were from the same stock as those used by Harkins and Myers² and by Harkins, Myers and Fowkes.³ The Finol, a Standard Oil product, did not spread when tested on the film balance and so was not purified further. The hexadecane purchased from the Eastman Company was kept over Fullers earth for several days. It was then distilled at a pressure of thirty millimeters of mercury, the central portion boiling at 270-271°C., uncorrected, was used.

The 60-70°C. ligroin, used to make all solutions, was purified with Fullers earth and redistilled.

Constant boiling hydrochloric acid was diluted to approximately one normal. It was then standardized. Aliquot parts

¹Ibid.

²Op. cit.

³Op. cit.

were taken to make approximately one-hundredth normal solution for the film substrate.

Both ordinary laboratory distilled water and water redistilled from potassium permanganate in a Pyrex still having a block tin condenser was used.

PROCEDURE

The procedure of a typical run was as follows. The trough was filled with doubly distilled water and the depth of the water adjusted until the cardioid condenser was in focus with the surface. Talc was used to make the surface visible. The surface was then swept thoroughly and the slide put in place. After the slide was in place the apparatus was closed, the balance beam lowered, and the air and water to the thermostat turned on. When equilibrium had been reached, a process which took about one hour, the calibration was checked. When the zero reading had been taken, the film was spread. Readings were taken every two minutes. The eight millimeter objective was used on the microscope almost exclusively as the four millimeter objective was much more difficult to focus and showed very little more detail. The air pump was shut off whenever a microscope observation was made, as, although there was not enough vibration to affect the reading of surface tension, there was enough to cause the objects in the field of the microscope to move with too high a speed.

It is important not to touch the slide with the fingers since that would contaminate it. It was therefore handled entirely by means of the wire clip by which it was attached to the copper wire that hung from the balance beam. Before immersion the slide was rinsed thoroughly with distilled water. The excess water was wiped off with a piece of filter paper and care taken to allow nothing to touch that portion of the slide which would be in the

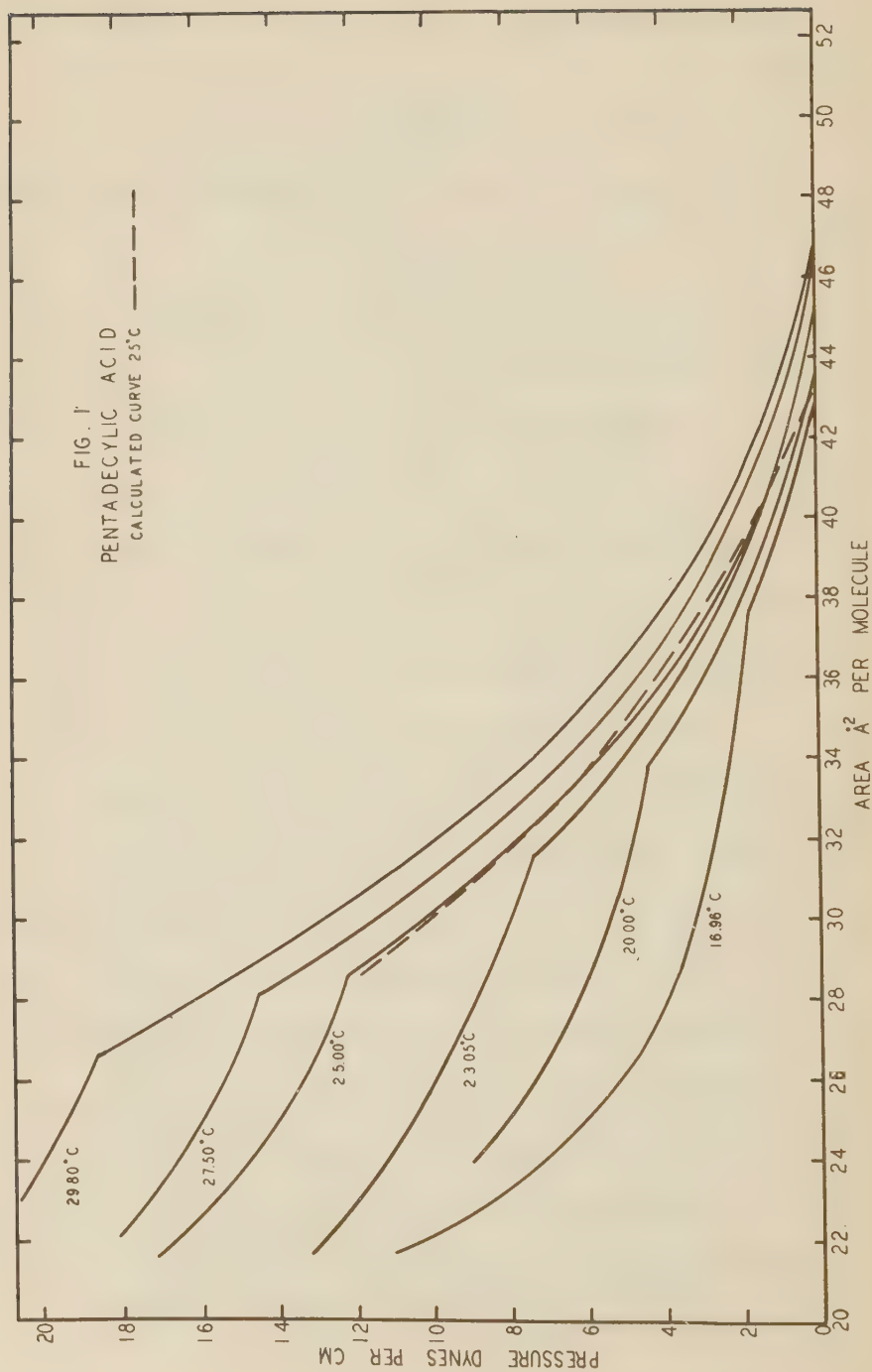
nothing to touch that portion of the slide which would be in the surface.

DISCUSSION

The force-area curves for pure pentadecylic acid at various temperatures are given in Fig. 1. These curves are very similar to the curves for myristic acid given by Adam and Jessop.¹ The area at half expansion for pentadecylic acid, however, comes at a considerably higher temperature.

An attempt was made to fit the Langmuir equation to the data for pentadecylic acid. The fitting of the experimental values to the equation was done by taking pairs of points along the curve and solving simultaneous equations for F_0 and a_0 . The variations in F_0 and a_0 with temperature as well as the change of the kink point are shown in Fig. 2. Fig. 2 shows that both a_0 and F_0 increase with an increase in the temperature, although F_0 does not increase nearly so fast. However, the value of both constants depends on the small difference between two large numbers divided by another small difference, which, coupled with the experimental error involved in determining the relative position of each curve with respect to the others, makes the values of a_0 and F_0 questionable. Referring to Fig. 1 again, the dotted curve represents the theoretical curve for twenty-five degrees. The discrepancy is believed to be much more than can be allowed because of experimental error and must, therefore, be attributed to the fact that the Langmuir equation is not the correct equation. This question as to the value of the constants can be brought out in another manner when the average value of a_0 is compared with the maximum and minimum values for a given experiment as is illus-

¹Proc. Roy. Soc., Series A, 120, 473 (1928).



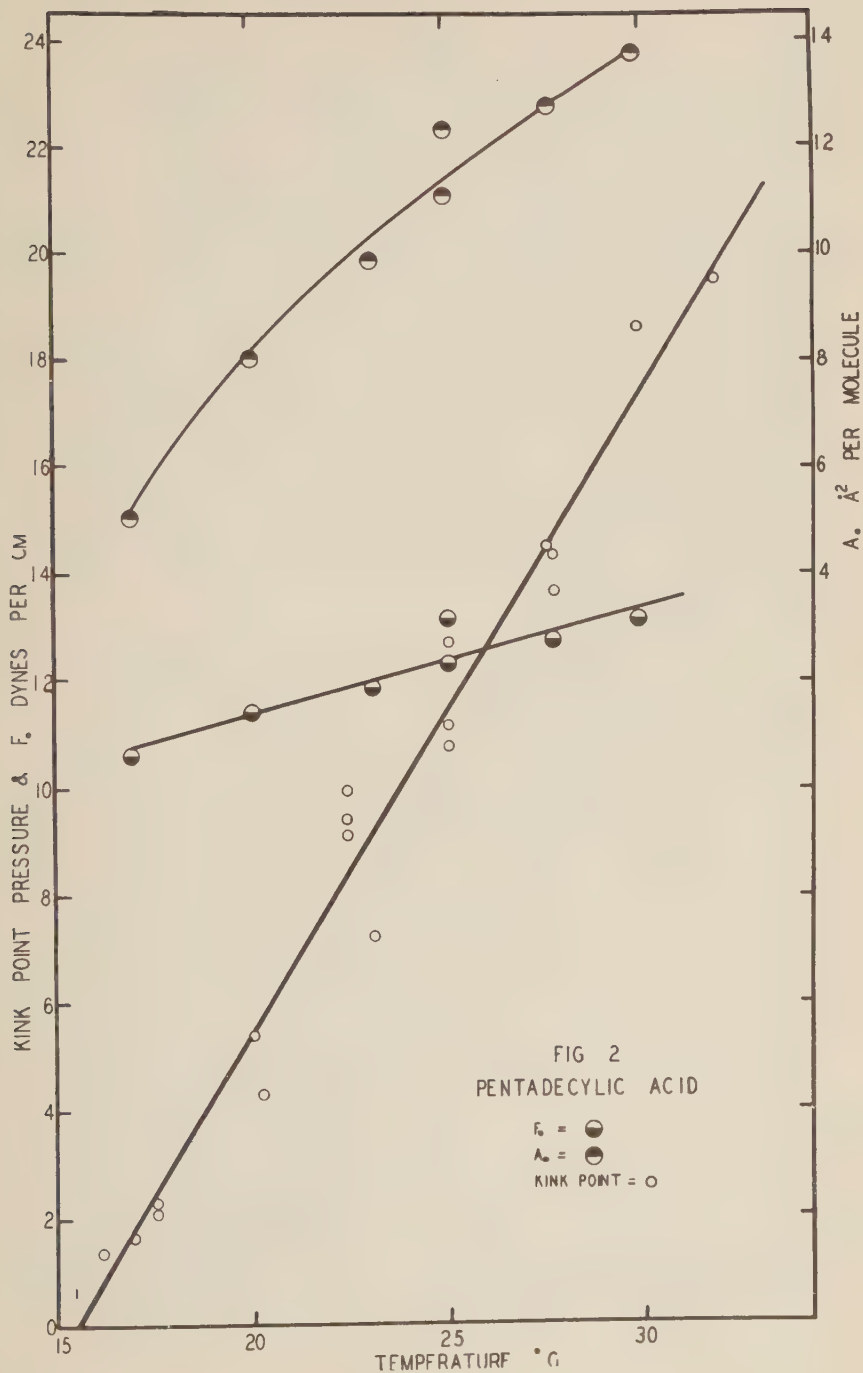


TABLE 1

Exp.	Temp.	a_0	a_0 Min.	a_0 Max.	F_0
112	16.96	5.44	5.01	5.87	10.62
113	20.00	8.02	6.20	9.40	11.44
114	23.05	9.86	7.49	11.42	11.85
118	25.00	12.35	10.59	13.14	13.17
105	25.00	11.09	10.89	11.63	12.31
115	27.50	12.76	10.54	13.58	12.79
116	29.80	13.77	12.69	14.09	13.15

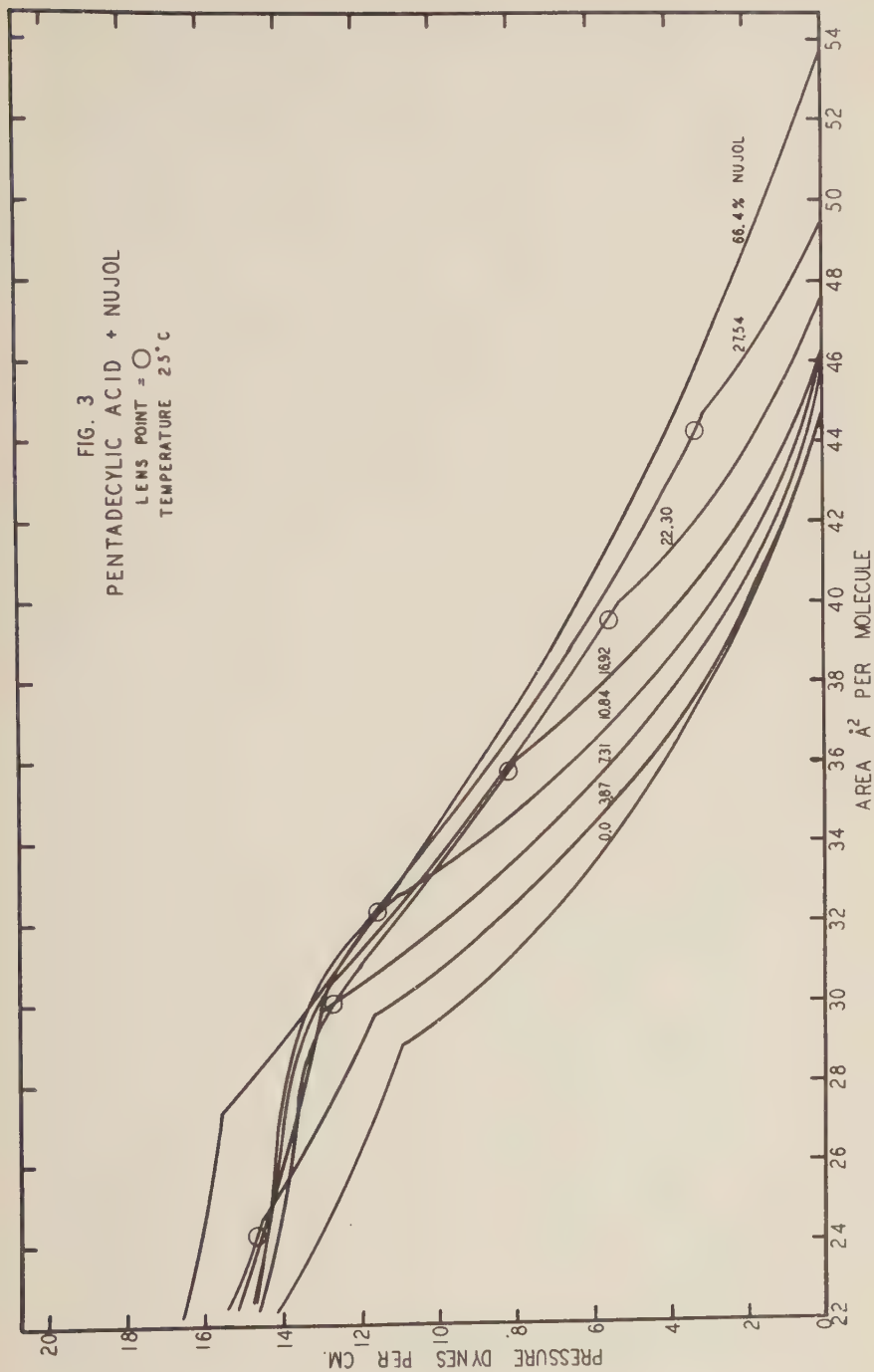
From the plot of kink point pressure against temperature, Fig. 2, it can be seen that there is a large random error in the position of the kink. It is believed that this random error is due not to experimental error but rather to factors which are at present unknown. The films are probably in a metastable state and dust particles, which are always present, may form a nucleus for some kind of change.¹

The force-area curves for various mixtures of pentadecylic acid and Nujol are given in Fig. 3. It is apparent that the addition of the oil causes a shift of the F-A curve to larger areas. If less than 33 per cent oil has been added, the F-A curve assumes, at low pressures, a shape similar to that of pure pentadecylic acid. However, a critical film pressure is reached in each case at which lenses suddenly appear, and the curve beyond this point is of a different character. The critical film pressure is lower with increase in oil content, which is in agreement with the results of Fowkes, Harkins and Myers² for myristic acid films. In the region of 33 per cent Nujol the film exhibited lenses at

¹In fact dust particles in the film are convenient for microscopic work as they allow focussing on the film when otherwise it would be invisible. This was shown in some work on cetyl alcohol films in which, by observing the Brownian movement of the dust, it was possible to check the point where the viscosity suddenly increased manyfold as determined by Dr. R. J. Myers in an unpublished work at the University of Chicago.

²Op. cit.

FIG. 3
PENTADECYLIC ACID + NUJOL
LENS POINT = O
TEMPERATURE 25°C



the start of the compression. Thus the 32 per cent point found by Harkins and Myers¹ corresponds to the critical concentration of Nujol beyond which the film is composite at all film pressures. This is shown in Fig. 4. The plot of the lens point pressure against the percentage of Nujol gives a straight line which extrapolates to 33.5 per cent Nujol at zero pressure and to 16 dynes at zero per cent Nujol.

Fig. 4 also gives the values of F_0 and a_0 for the mixed films calculated for the homogeneous part of the curves. It is interesting to note that if the value of -15.5 as the value of F_0 where the curve levels off is taken and the lens point curve extrapolated to zero value of F_{12} , the value 66.5 per cent oil is obtained. This is the value that Talmud and Talmud² give for the maximum adsorption of dry ammonium gas by a dried inverted film of palmitic acid and paraffin oil. Referring to Fig. 3, the curve for 66.4 per cent Nujol lies exactly where the 33.5 per cent curve would be expected. For all higher concentrations of oil Harkins and Myers³ have shown that the slope of the curve becomes much less as the concentration rises.

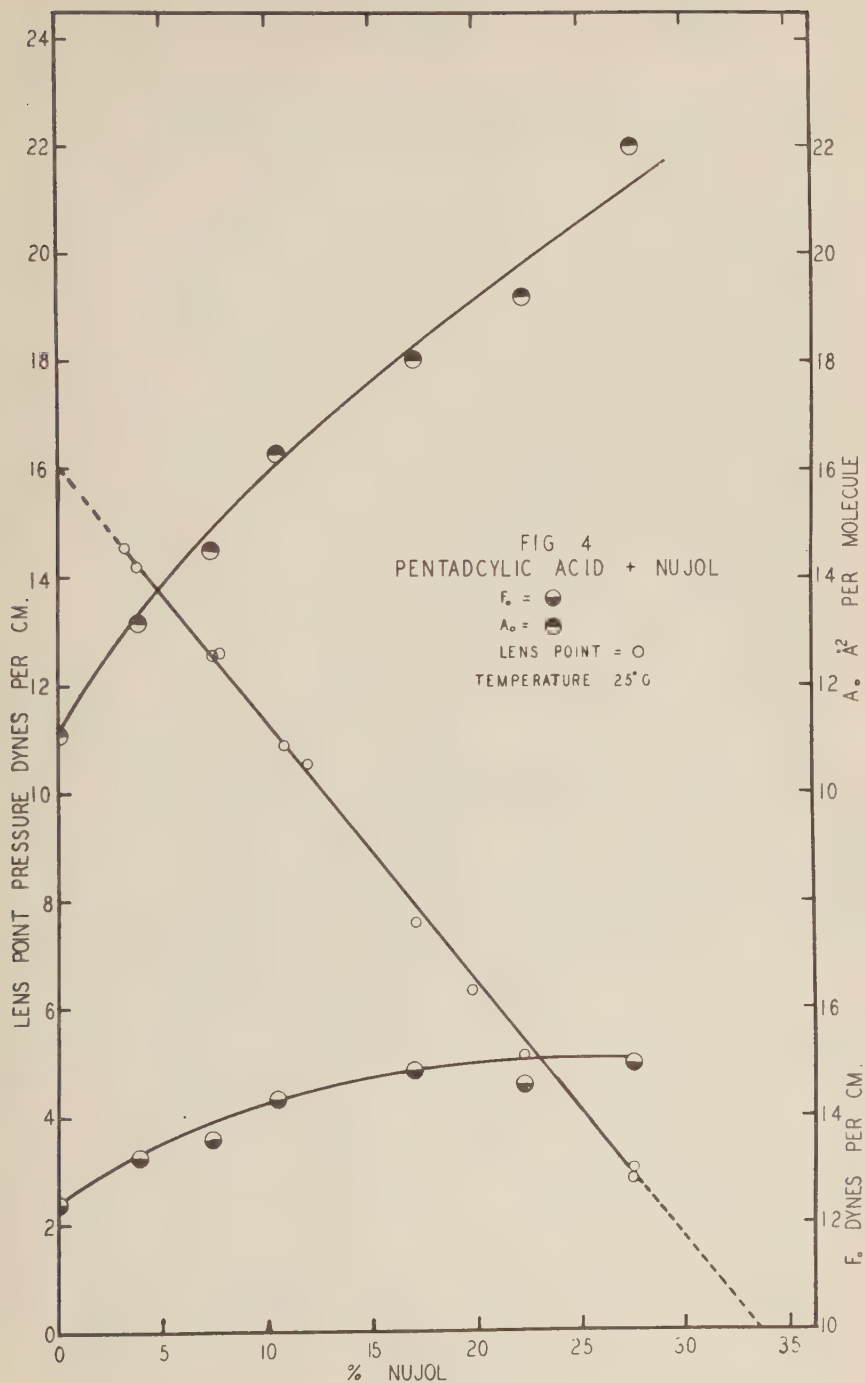
According to the theory outlined by Langmuir it would be expected that the value of a_0 would remain unchanged upon the addition of Nujol and the value of F_0 would vary linearly with the concentration. As Fig. 4 shows, neither of these expectations is fulfilled. It may be concluded, therefore, that for Nujol films the theory is not valid.

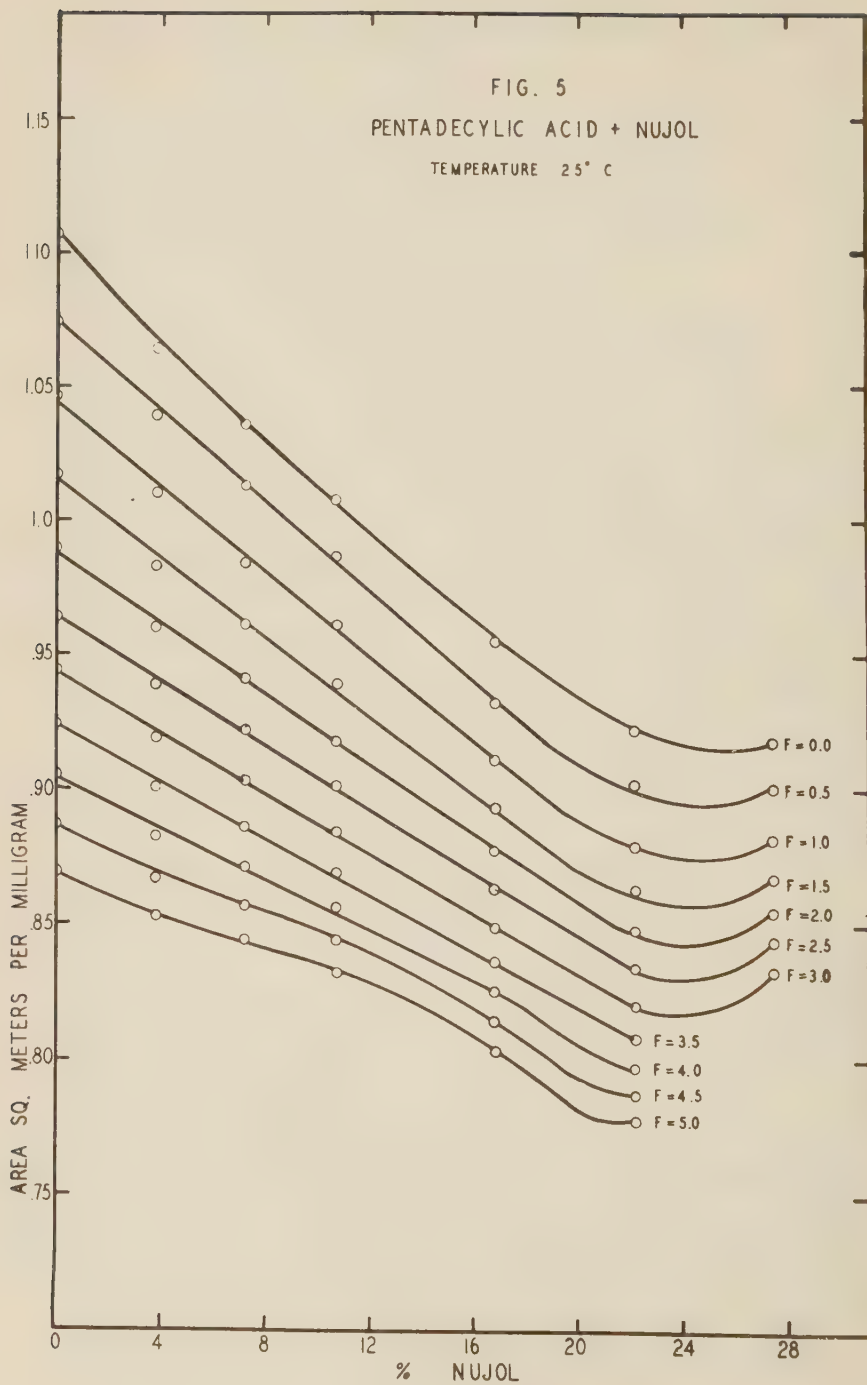
Fig. 5 shows isobars of area versus the percentage of Nujol. The area is expressed in square meters per milligram of mixture. The intercept on the zero per cent Nujol axis of the tangent to

¹Op. cit.

²Acta Physicochimica, 8, 171 (1938).

³Unpublished data, University of Chicago.

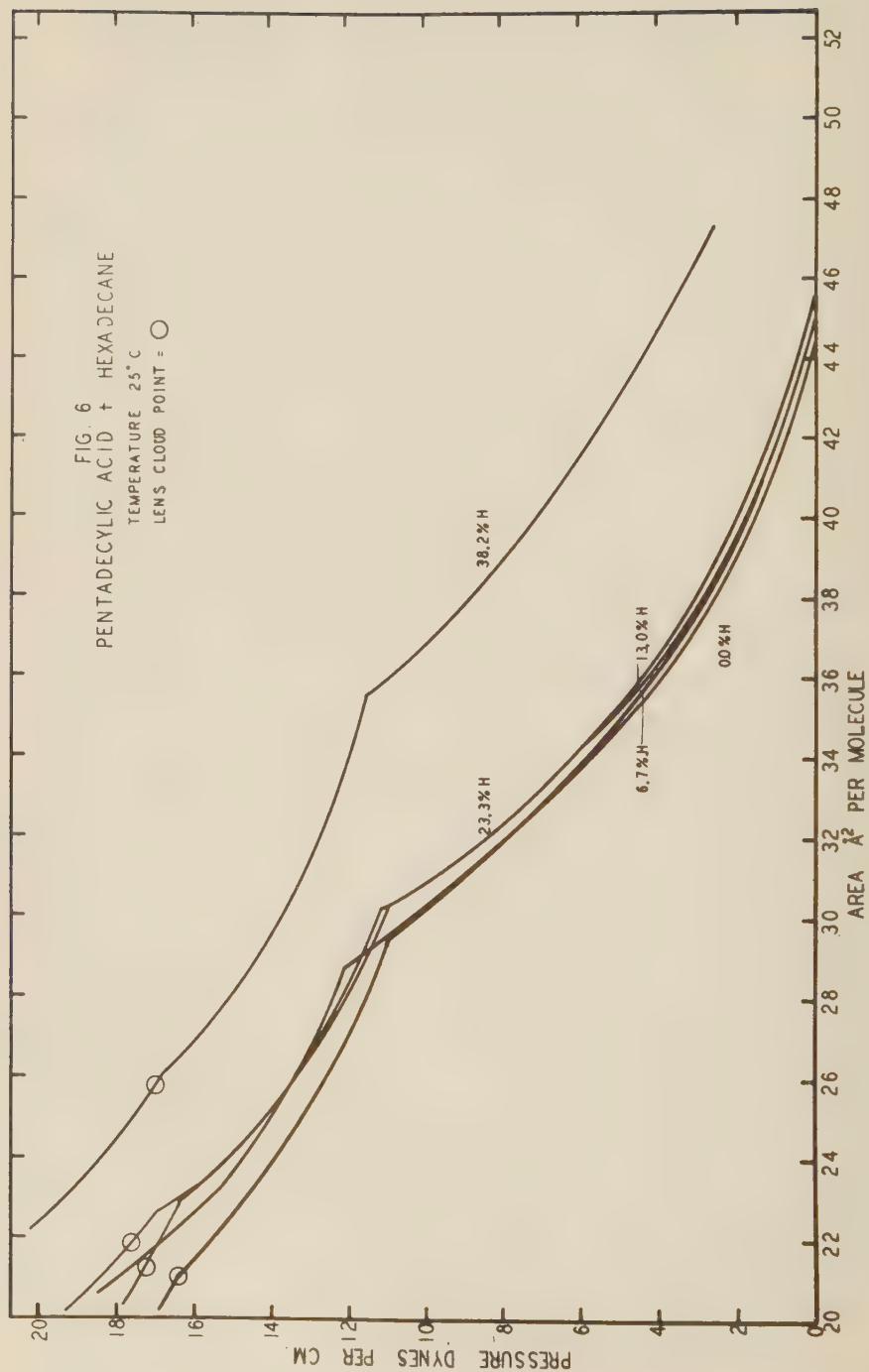




the curve thus gives the partial specific area of pentadecylic acid in the mixture. The intercept on the 100 per cent Nujol axis gives the partial specific area of the Nujol in the film. It is interesting to note that the partial specific area of the Nujol, i.e., the intercept of the tangent at 100 per cent Nujol, increases with the pressure, while that of the acid decreases and within the limits of error is the same as for the pure acid to quite large concentrations of oil. It will be noted also that, as the lens point is approached, the curves change slope rapidly and $\bar{a}_a$ decreases rapidly. It would be very much worth while if the accuracy of the experiments would be made great enough to determine just what the value is at the lens point. Higher pressures are not shown as the areas for the different curves are too close together. The force-area curves actually cross each other.

When a mixture of hexadecane and pentadecylic acid is compressed, there is no formation of lenses as with the Nujol mixtures. At the lens point, marked in Fig. 6, there is a sudden forcing out of a galaxy of very small lenses which usually group themselves in rough hexagonal rings of lenses. The value of F_0 for hexadecane and Nujol is probably not very different so that it is difficult to see how the Langmuir theory can account for the great difference in the two types of curves. It may be possible that the difference is due to the difference in the shape of the molecules. Nujol is known to consist largely of cyclic compounds, whereas, hexadecane is a normal straight chain hydrocarbon. This idea receives some confirmation in the fact that the curves for myristic acid with tetradecane and dotriacontane obtained by Harkins and Myers¹ have the same characteristics as the hexadecane and pentadecylic acid curves reported here.

¹J. A. C. S., 58, 1817 (1936).



The value of 16.5 dynes as the zero value of Nujol lens point led to the prediction that a condensed film, such as stearic acid which starts out at an area corresponding to the above force value for pentadecylic acid, would show lenses at all concentrations at zero pressure. A mixture of 4 per cent Nujol with stearic acid showed lenses at all pressures.

Mixtures of Nujol with myristic acid showed exactly the same behavior as did pentadecylic acid. The only difference when Finol was substituted for Nujol - pentadecylic and myristic acids were both investigated - was that the break in the curve at the lens point was not so sharp as when Nujol was present.

CONCLUSIONS

1. The equation given by Langmuir is not sufficiently accurate to describe the behavior of expanded films.

2. The theory developed by Langmuir cannot predict the behavior of mixed films.

3. A theory which takes into account the shape of the molecules of added hydrocarbon is necessary.

4. The concepts embodied in F_0 and a_0 do describe certain properties of expanded films, and some function of these parameters is necessary to a complete theory.

5. A pentadecylic acid-Nujol film is non-homogeneous above 33.5 per cent oil.

